Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

WSC – CAM – III D

Quality Assurance and Quality Control Requirements and Performance Standards for *SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)* for the Massachusetts Contingency Plan (MCP)

Document Status: Final

Donald Muldoon
Department of Environmental Protection
One Winter Street
Boston, MA 02108

donald.muldoon@state.ma.us

Document Chronology

Revision	Status	Date
0	Public Comment Draft	20 December 2002
1	Final	30 May 2003
2	Final	13 August 2004

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

III   Trace Metal Analyses

D.   QA/QC Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by ICP-MS

Table of Contents

List of Tables, Appendices and Exhibits

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

1.0 QA/QC Requirements for SW-846 Method 6020A

1.1 Method Overview

Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of trace elements (including metals) at sub-µg/L concentrations in solution. The method is applicable to all of the analytes listed in Table III D-2 as well as numerous other elements (refer to SW-846 Method 6020A, Table III D-4). Until very recently, ICP-MS has most often been used to exploit the method's sensitivity and specificity as compared to more conventional trace metal analytical techniques. The most common application of this method has been in support of ecological risk assessments and in place of graphite furnace atomic absorption techniques. Recent advances in both instrumentation and software have improved the overall performance and ruggedness of ICP-MS to a point where it has become the instrument of choice for even routine trace metal analytical applications in a growing number of laboratories.

Acid digestion prior to analysis is required for all matrices (groundwater, wastes, soils, sediment, etc.), for which total (acid-leachable) elements are required, except for dissolved metals. Samples for dissolved metals are first filtered and then acid-preserved prior to analysis. Refer to Chapter 3.0, SW-846 for the appropriate digestion procedures.

1.1.1 Reporting Limits for SW-846 Method 6020A

Reporting Limits (RL), sensitivity, and the optimum and linear concentration ranges of the analytes can vary with the mass spectrometer, matrix, and operating conditions. In relatively simple matracies, reporting limits will generally be below 0.1 µg/L for most elements. Reporting limits for less sensitive elements such as arsenic and selenium and desensitized major elements may be 1.0 µg/L or higher. The isotopic masses recommended for quantitation of selected elements are presented in Table 3, SW-846 Method 6020A.

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, and sediment matrices for trace metals analyzed in support of MCP decision-making are presented in Appendix III A–1 of this document and Appendix VII-A, WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data in Support of Response Actions Conducted Under the Massachusetts Contingency Plan (MCP)".

1.1.2 General Quality Control Requirements of SW-846 Method 6020A

Each laboratory that uses SW-846 Method 6020A s required to operate a formal quality assurance program to demonstrate the precision and bias of the method as performed by the laboratory and procedures for determining the method reporting limit (RL). The minimum requirements of this program consist of an initial demonstration of laboratory proficiency, ongoing analysis of standards and blanks as a test of continued performance, and the analysis of laboratory control samples (LCSs), and LCS duplicates to assess accuracy and/or precision. Project-specific matrix duplicates

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

or matrix spike duplicates (MSDs) may be used in lieu of LCS duplicates to evaluate precision when such samples are analyzed either at discretion of laboratory or at request of data-user.

Laboratories must document and have on file an Initial Demonstration of Capability for each combination of sample preparation and determinative method being used. These data must meet or exceed the performance standards as presented in Section 1.4 and Table III D-1 of this method. Procedural requirements for performing the Initial Demonstration of Capability can be found in SW-846 Chapter One, Section 4.4.1 and SW-846 method 6020A, Section 8.0. The data associated with the Initial Demonstration of Capability must be kept on file at the laboratory and made available to potential data-users on request. The data associated with the Initial Demonstration of Capability for SW-846 Method 6020A must include the following:

QC Element	Performance Criteria
Initial Calibration	WSC-CAM-III D, Table III D-1
Continuing Calibration	WSC-CAM-III D, Table III D-1
Method Blanks	WSC-CAM-III D, Table III D-1
Percent Recovery for MS/LCS	WSC-CAM-III D, Table III D-1
Relative Percent Difference (RPD) for MSD/LCS Duplicate	WSC-CAM-III D, Table III D-1
Other Instrument QC Samples	WSC-CAM-III D, Table III D-1

It is essential that laboratory-specific performance criteria for LCS, LCS duplicates (or project-specific matrix duplicates or matrix spike duplicates, see Table III D-1) and the other data quality indicators, listed in Table III D-1, also be calculated and documented. When experience indicates that the criteria recommended in specific methods are frequently not met for some analytes and/or matrices, the in-house performance criteria will be a means of documenting these repeated exceedances. Laboratories are encouraged to actively monitor pertinent quality control performance standards described in Table III D-1 to assess analytical trends (i.e., systematic bias, etc) and to improve overall method performance.

For SW-846 Method 6020A, laboratory-specific control limits must meet or exceed (demonstrate less variability than) the performance standards for each QC element listed on Table III D-1. It should be noted that the performance standards listed in Table III D-1 are based on multiple-laboratory data, which are in most cases expected to demonstrate more variability than performance standards developed by a single laboratory. Laboratories are encouraged to continually strive to minimize variability and improve the accuracy and precision of their analytical results. The LSP will utilize this analytical performance data to verify that the results reported by the laboratory are consistent with the pre-established data quality objectives for the disposal site.

This method is restricted to use by, or under the supervision of spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences described in this method and the analysis of environmental samples using ICP-MS.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

1.2 Summary of Method

This method describes multi-elemental determinations by ICP-MS in environmental samples. The method measures ions produced by a radio-frequency ICP. Liquid samples are nebulized and the resulting aerosol is transported by argon gas to the plasma torch of the ICP and ionized. The resultant ions are introduced into the mass spectrometer where they are sorted according to their mass-to-charge ratios and quantified. Interferences must be assessed and valid corrections applied (see Section 1.3, below). Interference corrections must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

1.2.1 Sample Preparation

Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods as described in Chapter 3.0, SW-846 (e.g., methods 3005-3051) and summarized in Appendix III D-2, *Methods for Sample Digestion or preparation for Metal Analyses by ICP-MS.* When analyzing groundwater samples for dissolved constituents, acid digestion is not necessary if the samples are first filtered and then acid preserved prior to analysis.

1.2.2 Internal Standards

An appropriate internal standard (IS) is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi; however, experienced analysts should choose an IS based on mass and IP for the metals of interest. Preparation of the recommended internal standard stock solutions is described in SW-846 method 6020A, Sections 7.3.1 through 7.3.10, respectively. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interferences from native lithium are minimized. Other elements may need to be used on occasions when samples contain native concentrations of the recommended internal standards.

1.2.3 Additional Quality Control Monitoring

To obtain data of known quality, it is necessary to measure more than the analytes of interest. Potential interferences must also be monitored continuously in order to apply appropriate corrections or to determine whether such corrections are warranted at all. Extensive quality control (QC) monitoring to evaluate the necessity for interference corrections are required at all times for ICP-MS. Refer to Table III D-1 (Specific QA/QC Requirements and Performance Standards for MCP SW846 Method 6020A), herein and to Section 9.0, Quality Control, of SW846 Method 6020A for further details on QC samples.

1.3 Method Interferences

Interferences must be assessed for ICP-MS. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix. Interferences can include: isobaric elemental interferences, isobaric molecular interferences, doubly-charged ion interferences, physical interferences, and memory interferences.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Types of interferences and approaches for minimizing their adverse effects are described in detail in Section 4.0, SW-846 Method 6020A, and summarized herein. Tests for the evaluation of potential method interferences are also described in Section 8.0, SW-846 Method 6020A. Types of common interferences on ICP-MS include:

➢ Isobaric elemental interferences (described in Section 4.1 of SW-846 Method 6020A) – caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio. A data system must be used to automatically correct for these interferences by determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal.

➢ Isobaric molecular interferences and doubly-charged ion interferences (described in Section 4.2 of SW-846 Method 6020A) – caused by ions consisting of more than one atom or charge, respectively. Isobaric interferences that affect ICP-MS results are identified in the literature. A common example of isobaric molecular interference is from chloride on arsenic (specifically, $ArCl^+$ on ^{75}As). Molecular isobaric interferences can be corrected using the natural isotope abundances from the literature. For most commercial ICP-MS instruments, this correction based on the natural isotope abundances is automatically performed by the data system. See Section 4.2 of SW-846 Method 6020A for example isobaric corrections and Section 9.4 of SW-846 Method 6020A for further information on isobaric interferences. The adequacy of corrections for isobaric interferences is partly evaluated through the use of the interference check solutions (ICSA and ICSAB, see Table III D-1).

In addition, solid phase chelation, as described in SW-846 Method 6020A, Section 4.3, may also be considered as an option to eliminate isobaric interferences from both elemental and molecular sources.

➢ Physical interferences (described in Section 4.4 of SW-846 Method 6020A) – caused by sample viscosity and surface tension affect on the sample nebulization. Samples with high dissolved solids or high acid content can exhibit physical interference.

   Analytical Note: Dissolved solids, deposited on the nebulizer tip and/or interface skimmers during sample processing will adversely affect instrument performance. A final total solids concentration below 0.2% (2000 mg/l) is recommended to optimize system performance.

Physical interferences can be minimized by using an internal standard (IS). The internal standard corrects for physical interferences but must meet the QC acceptance criteria listed in Table III D-1 (the intensity level of an internal standard must be greater than 30% and less than 120% of the intensity of the first standard used during calibration). If the IS falls outside the QC window, then dilution is required.

➢ Memory interferences (described in Section 4.5 of SW-846 Method 6020A) – caused by a high concentration sample contributing to signal of subsequent sample. Memory interferences can be minimized by using rinse blanks for appropriate rinse times between all sample analyses.

		WSC-CAM	Section: III D
	Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup	13 August 2004	Revision No. 2
		Final	Page 7 of 23

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

➢ High salt concentrations (e.g., seawater samples) – cause analyte signal suppression or enhancement, dependent upon the element. Samples with high salt content can cause both physical interference and isobaric molecular interferences (as with the chloride interference on arsenic described above, which can result in biased high arsenic results). IS must be used for all samples and samples should be diluted to bring the sodium (and other analytes) within the linear range of the instrument. Note, however, that this approach (dilution) may raise the sample-specific reporting limit for analytes of interest above the MCP requirements. Therefore, it is recommended that alternate preparation/extraction methods be used to remove significant salt interference prior to ICP-MS analysis.

1.4 Quality Control Requirements for SW-846 Method 6020A

1.4.1 General Quality Control Requirements for Determinative Inorganic Methods

Refer to SW-846 Chapter One for general quality control procedures for all inorganic methods, including SW-846 Method 6020A. These requirements ensure that each laboratory maintain a formal quality assurance program and records to document the quality of all inorganic data.

Quality Control procedures necessary to evaluate the instrument's operation may be found in Chapter One, Section 2.0, and include evaluation of calibrations and performance of sample analyses.

Instrument quality control and method performance requirements for the ICP-MS system may be found in SW-846 Method 6020A, Sections 9.0 and 10.0, respectively and are described graphically in Appendix III D-3.

1.4.2 Specific QA/QC Requirements and Performance Standards for MCP SW-846 Method 6020A

Specific QA/QC requirements and performance standards for SW-846 Method 6020A are presented in Table III D-1. Strict compliance with the QA/QC requirements and performance standards for this method, as well as satisfying other analytical and reporting requirements will provide a data user with "Presumptive Certainty" regarding the usability of analytical data to support MCP decisions. The concept of "Presumptive Certainty" is explained in detail in Section 2.0 of WSC-CAM-VII A.

While optional, parties electing to utilize these protocols will be assured of "Presumptive Certainty" of data acceptance by agency reviewers. In order to achieve "Presumptive Certainty", parties must:

a) Comply with the procedures described and referenced in WSC-CAM–III D;

b) Comply with the applicable QC requirements prescribed in Table III D-1 for this test procedure;

c) Evaluate, and narrate, as necessary, compliance with performance standards prescribed in Table III D-1 for this test method; and

d) Adopt the reporting formats and elements specified in the CAM.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

In achieving the status of "Presumptive Certainty", parties will be assured that analytical data sets:

- ✓ Will satisfy the broad <u>QA/QC requirements</u> of 310 CMR 40.0017 and 40.0191 regarding the scientific defensibility, precision and accuracy, and reporting of analytical data;

- ✓ May be used in a <u>data usability</u> assessment, and if in compliance with all MCP Analytical Method standards, laboratory QC requirements, and field QC recommended limits and action levels, the data set will be considered useable data to support site characterization decisions made pursuant to the MCP; and

- ✓ May be used to help support a <u>data representativeness</u> assessment.

Widespread adherence to the "Presumptive Certainty" approach will promote inter-laboratory consistency and provide the regulated community with a greater degree of certainty regarding the quality of data used for MCP decision-making. The issuance of these requirements and standards is in no way intended to preempt the exercise of professional judgement by the LSP in the selection of alternative analytical methods. However, parties who elect not to utilize the "Presumptive Certainty" option have an obligation, pursuant to 310 CMR 40.0017 and 40.0191(2)(c), to demonstrate and <u>document</u> an overall level of (laboratory and field) QA/QC, data usability, and data representativeness that is adequate for and consistent with the intended use of the data.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Preparation of Samples and Standards	Accuracy and Representativeness	All aqueous and solid samples must be prepared prior to analysis for total (acid-leachable) elements, with the exception of aqueous samples filtered for dissolved metals analysis. See Appendix III D-2 for appropriate digestion methods. Standards should be matrix-matched using Type 1 water and appropriate acid concentrations to be consistent with the digested samples.	No		
Daily Performance Standard	Accuracy	(1) Frequency – Daily prior to tuning and when instrument modifications performed (2) Daily performance standard should be a 10 μg/L standard of 3 or more elements representative of the analytical mass range. (3) Purpose – check of sample introduction; sensitivity; oxide and double charge interferences. This is a multiple check on instrument performance suggested by the manufacturers. (4) Criterion: < 3%		If Daily Performance Standard exceeds 3% criterion; perform instrument maintenance and re-run standard.	If data are reported from an ICP-MS run in which the Daily Performance Standard exceeded 3%, lab must narrate why the data are considered valid.
Tuning	Accuracy - Verify Operating Conditions	(1) Frequency – Daily prior to calibration (2) Tuning solution must contain elements representing all of the mass regions of interest (see Method 6020A Section 5.8) (3) Criteria: Mass Calibration $\leq$ 0.1 amu difference from true; Resolution < 0.9 amu full width at 10% peak ht; (4) Relative Standard Deviation (RSD) $\leq$ 5%	No	Re-optimize instrument operating conditions, re-tune	Suspend all analyses until tuning non-compliance is rectified

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Initial Calibration	Laboratory Analytical Accuracy	(1) Frequency - Daily following tuning of ICP-MS and prior to sample analysis. Also required if any modifications are made to the sample introduction system or detectors. (2) A minimum of 3 non-blank calibration points which may include the RL and the LR standard. If RL or LR standards not included in calibration curve, then RL and LR check standard QC samples are required (see below). (3) Minimum of 3 integrations for calibration and sample analyses (4) Linear curve fit with correlation coefficient r > 0.995.	No	Re-optimize instrument set up; re-calibrate as required by method.	(1) Sample analysis cannot proceed without a valid initial calibration for all elements being reported. (2) If linear regression is not used for analyte quantitation (e.g., use of a quadratic equation), this must be noted in the case narrative with a list of the affected analytes.
Initial Calibration Verification (ICV)	Laboratory Analytical Accuracy	(1) Frequency - Daily immediately after initial calibration (2) Separate-source (independent) from calibration standards; matrix-matched (same acid matrix as standards and samples); near midpoint of calibration curve. (3) ICV % recovery must be 90-110%	No	Re-calibrate/Re-analyze ICV as required by method	Suspend all analyses until Initial Calibration non-conformance is rectified.
Initial Calibration Blank (ICB)	Laboratory Analytical Sensitivity (instrument drift and contamination evaluation)	(1) Frequency - Daily immediately after ICV (2) Must be matrix-matched (the same concentration of acids as standards and samples) (3) ICB must be < Reporting Limit (RL)	No	Re-calibrate/Re-analyze ICB as required by method	
Reporting Limit (RL) Calibration Check Standard	Laboratory Analytical Sensitivity (to support the RL)	(1) Frequency – Required daily, following initial calibration, only if RL standard not included in initial calibration curve. (2) Check Standard at the level of the RL for all analytes (RL must be ≤ ½ MCP Method 1 Cleanup Standard for each metal; or < applicable site-specific RL (based on project DQOs) 3) Criteria: % recovery 70-130%	No	Re-calibrate / re-analyze or narrate if affected elements are detected in samples at > 10x level of the RL	This is a MADEP-MCP required performance standard to verify the RL when a multi-point calibration does not include the RL standard.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Continuing Calibration Verification (CCV)	Laboratory Analytical Accuracy	(1) Frequency - Every 10 analytical samples and at end of run (2) Same-source as calibration standards; near mid-point of calibration curve (3) CCV % recovery must be 90-110%	No	Terminate analysis, correct the problem, and re-calibrate and then re-analyze all samples since last compliant CCV.	Narrate non-compliance.
Continuing Calibration Blank (CCB)	Laboratory Analytical Sensitivity (instrument drift and contamination evaluation)	(1) Frequency - Every 10 samples and at end of run immediately after CCV (2) Must be matrix-matched (the same concentration of acids as standards and samples) (3) CCB must be < $\pm$RL (i.e., negative drifts > -RL and positive values > +RL are non-compliant).	No	If associated sample results are > 10x CCB level; accept results. If not, re-calibrate and then re-analyze all samples since last compliant CCB.	Narrate non-compliance.
Linear Range (LR) Check Standard	Laboratory Analytical Accuracy	(1) Frequency – Required daily following the initial calibration, only if a standard at the level of the linear range is not included in the calibration curve. (2) Criteria: recovery 90-110% of true value.	No	Re-optimize instrument set up; re-calibrate as required by method.	Narrate non-compliance.
Interference Check Solutions (ICS A and ICSAB)	Laboratory Analytical Accuracy – verify adequacy of isobaric interference corrections	(1) Frequency – Daily at beginning of analytical run (2) ICS A and ICSAB contain known amounts of interferents and analytes (see Method 6020A section 5.6) (3) Criteria: % recoveries 80-120%	No	This is a method requirement of SW-846 6020A. No corrective action required because instrument corrections are based on natural isotope abundances that cannot be changed.	Narrate non-compliance. If IS in compliance, then data are acceptable.
Method (Preparation) Blank	Laboratory Method Sensitivity (contamination evaluation)	(1) Frequency – One per digestion batch of $\leq$ 20 field samples. If samples undigested (dissolved metals) the ICB serves as the method blank. (2) Must be matrix-matched (the same concentration of acids as calibration and QC standards) and digested with the samples (3) Method Blank must be < RL	Yes	Re-digest/Re-analyze all associated samples unless all detected results are > 10x method blank level.	Narrate non-compliance.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Laboratory Control Sample (LCS)	Laboratory Method Accuracy	(1) Frequency - One per digestion batch of ≤ 20 field samples. If samples are undigested (dissolved metals) the ICV = LCS. (2) LCS must be matrix-matched to samples (aqueous/solid) and digested with the samples (3) LCS % recoveries for all analytes must be 80-120% for aqueous media and vendor control limits (95% confidence limits on a standard reference material) for solids.	Yes	Re-digest/Re-analyze all associated samples.	Narrate non-compliance.
LCS Duplicate	Laboratory Method Precision	(1) Frequency - One per digestion batch of ≤ 20 field samples. If samples are undigested (dissolved metals) an ICV duplicate may be substituted for an LCS duplicate. (2) LCS duplicate must be matrix-matched to samples (aqueous/solid) and digested with the samples (3) Prepared using same standard source and concentration as LCS. (4) Recommended to be run immediately after LCS in analytical sequence. (5) Laboratory–determined Relative Percent Difference (RPD) must be ≤ 20 (aqueous) and ≤ 30 (solids), and (6) A project-specific MD or MSD may be substituted to evaluate precision in lieu of an LCS duplicate.	Yes	Recalculate RPD; Locate source of problem; Narrate non-conformances	(1) Locate and rectify source of non-conformance before proceeding with the analyses of subsequent sample batches. (2) Narrate non-conformances
Project-Specific Matrix Spike Sample (MS)	Method Accuracy in Sample Matrix	(1) Frequency - One per digestion batch of ≤ 20 field samples if requested by data user. If samples are undigested (dissolved metals) perform an analytical spike. (2) MS % recoveries for all analytes: 75-125% for all media.	Yes Only when requested by the data-use	If MS % recovery is > 30%, and LCS was in-control, no corrective action is required. If MS %recovery is < 30%, and non-detected results were found, one or more of the following may be performed to confirm matrix effect: 1) homogenize sample well, re-digest, and re-analyze sample/MS; 2) perform method of standard additions for quantitation; 3) perform post-digestion spike.	Narrate non-compliance. Note to data users: USEPA Region I data validation guidance requires rejection of non-detected results with MS <30% recovery. Therefore, the 1st corrective action listed may be required for critical sample data to obtain usable results.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Project-specific Matrix Duplicate Sample (MD) or Matrix Spike Duplicate (MSD)	Method Precision in Sample Matrix	(1) Frequency - One per digestion batch of < 20 field samples at discretion of laboratory or at request of data user. If samples are undigested (dissolved metals) perform an analytical duplicate. (2) MD or MSD relative percent difference (RPD): aqueous results > 5x RL:+20%; aqueous results < 5x RL difference < RL; solid results > 5x RL: + 35%; solid results < 5x RL: difference < 2x RL.	Yes Only when requested by the data-use	No corrective action required, narrate.	Narrate non-compliance. Note: acceptance criteria consistent with USEPA Region I data validation guidance.
Dilution Test	Accuracy in Sample Matrix	(1) Frequency – one dilution test for every 20 field samples; only if analyte is > 100x RL (2) Dilution test = 5x dilution (3) Difference criterion + 15%	No	None.	Narrate non-compliance.
Internal Standards	Analytical Accuracy in Sample Matrix	(1) Frequency – Internal Standards must be added to each field sample and QC sample. (2) Field Samples – Relative Intensity (RI) of IS (RI in %) must be 30-120% of IS in original calibration. (3) QC Samples – RI must be 80-120%. (4) Optimize mass and ionization potential match of IS to elements that will be quantitated by ICP-MS. See method 6020A for recommended IS elements and further details.	No	Perform dilution and re-analyze until IS criteria met. If still not met, terminate analysis, re-calibrate, verify new calibration, and reanalyze affected samples.	Narrate non-compliance.
Initial Demonstration of Capability	Laboratory Method Sensitivity (to support the RL), accuracy, precision	Frequency - Perform IDP for all elements on ICP-MS once to show method proficiency (MADEP requirement). Requires successful initial calibration, all QC stated herein, method blank, LCS, MS, MSD and/or MD.	No	Not applicable.	IDC data must be kept on file to document initial demonstration of performance (IDP) for each ICP-MS element and instrument.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Required QA/QC	Data Quality Objective	Performance Standard	Required Deliverable	Recommended Corrective Action	Analytical Response Action
Sample Quantitation and General Reporting	NA	(1) Non-detected values must be reported with the sample-specific reporting limit for each analyte. (2) The RL should be ≤ the Method 1 Cleanup Standard for each metal or < the project-specific RL determined during DQO process (e.g., to support human health or ecological risk assessment). (3) The RL must be supported by either including it in the multi-point calibration curve or verified using a daily RL check standard, following the calibration curve. (4) Results for solid matrices must be reported on a dry-weight basis to compare to MCP standards. (5) Sample concentrations that exceed the LR of the instrument (LR determined either by including LR standard in calibration curve or analyzing the daily LR check standard) must either be diluted (in the same acid matrix) or measured at an alternate (less abundant) isotope to fall within the linear range when re-analyzed, or reported with narration. (6) All concentration calculations must include appropriate interference corrections as described in SW-846 Method 6020A, Section 4.2, internal standard normalization, and appropriate compensations for isotopic abundances (e.g., requirements for lead). A flow chart summarizing QC requirements for SW-846 Method 6020A ICP-MS analysis is presented in Appendix III D-3.	Yes	Not applicable.	Narrate any additional method non-compliance or sample-specific anomaly.

Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup	WSC-CAM	Section: III D
	13 August 2004	Revision No. 2
	Final	Page 15 of 23

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

1.5 List of Analytes for SW-846 Method 6020A

The MCP analyte list for SW-846 Method 6020A presented in Table III D-2, is intended to be protective of human health and the environment and the Commonwealth's groundwater resources. The list is comprised potential toxic metal contaminants that are readily-analyzable by SW-846 Method 6020A and have a Method 1 Groundwater/Soil Standards as described in 310 CMR 40.0974.

The MCP Method 1 Groundwater/Soil Standards used to characterize the risk of harm posed by oil or hazardous materials at a disposal site are described in 310 CMR 40.0974(2), Table 1. This list of groundwater/soil standards, developed by the Department, takes into account a defined set of conservative potential exposure pathways likely to be encountered at most disposal sites. Method 1 Standards have been developed by the Department for over one hundred organic and inorganic contaminants that are commonly encountered at disposal sites. The MCP Method 1 Groundwater/Soil Standards list is continually reviewed and updated by the Department. When compounds are added to the MCP Method 1 Groundwater/Soil Standards list that are suitable for analysis by SW-846 Method 6020A, the analyte list for this method will be updated accordingly.

1.6 Additional Analyte Reporting Requirements for SW-846 Method 6020A

1.6.1 Analysis and Reporting Recommendations for SW-846 Method 6020A to Demonstrate Compliance with MCP Cleanup Standards

While it is not necessary to request and report all the SW-846 Method 6020A analytes listed in Table III D-2 to obtain Presumptive Certainty, it is necessary to document such a limitation, for site characterization and data representativeness considerations. DEP strongly recommends use of the full analyte list during the initial stages of site investigations, and/or at sites with an unknown or complicated history of uses of oil or hazardous materials. These assessment activities may include but are not limited to:

- ✓ Immediate Response Actions (IRAs) performed in accordance with 310 CMR 40.0410;
- ✓ Initial Site Investigation Activities performed in accordance with 310 CMR 40.0405(1);
- ✓ Phase I Initial Site Investigation Activities performed in accordance with 310 CMR 40.0480 through 40.0483; and
- ✓ Phase II Comprehensive Site Investigation Activities performed in accordance with 310 CMR 40.0830

In a limited number of cases, the use of the full analyte list for a chosen analytical method may not be necessary, with respect to data representativeness concerns, including:

- ✓ Uncharacterized sites where substantial site/use history information is available to rule-out all but a limited number of contaminants of concern, and where use of the full analyte list would significantly increase investigative costs; or
- ✓ Well-characterized sites where initial full-analyte list testing efforts have sufficiently narrowed the list of contaminants of concern.

	Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup	WSC-CAM	Section: III D
		13 August 2004	Revision No. 2
		Final	Page 16 of 23

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Note that a desire to avoid detection and quantitation of a contaminant that is present or likely present at a site above background levels is not a valid reason to limit an analyte list, and that such an action could constitute a criminal violation of MGL c. 21E.

In cases where a truncated list of method analytes is selected, laboratories must still employ the method-specific quality control requirements and performance standards associated with the requested analytes list to obtain Presumptive Certainty status.

1.6.2 Analysis and Reporting recommendations for SW-846 Method 6020A to Support Ecological Risk Assessments Under the MCP

For many applications, SW-846 Method 6020A is the preferred analytical approach for the determination of toxic metals in various environmental media to support ecological risk assessment decisions under the MCP. This method has the requisite sensitivity and flexibility to cost-effectively identify and quantify a wide range of ecologically-significant elements. The data user should consult with the ecological risk assessor to develop data quality objectives for the sampling program to include contaminants of concern and program-specific reporting limits. Any non-routine modifications to the method must be described in the Environmental Laboratory case narrative.

1.6.3 Additional Analyte Reporting Requirements for Mercury using SW-846 Method 6020A

Mercury is not included on the standard analyte list for SW-846 Method 6020A because of the special requirement for sample digestion and processing necessary to produce valid data. Mercury data based on SW-846 Method 6020A may be used in support of MCP Response Actions, however, if the sample digestion and processing precautions described in SW-846 Method 6020A, Section 11.1 are satisfied, and the overall quality control and performance standards for the method are met.

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Table III D-2 Analyte List for SW-846 Method 6020A

Analyte	CASRN	MCP METHOD 1 STANDARD	
		GW-1	S-1/GW-1
		µG/L (PPB)	mG/KG (PPM)
Antimony[1]	7440360	6	10
Arsenic	7440382	50	30
Barium	7440393	2000	1000
Beryllium	7440417	4	0.7
Cadmium	7440439	5	30
Chromium (Total)	7440473	100	200
Lead	7439921	15	300
Nickel	7440020	80 (GW-3) 100 (GW-1)	300
Selenium	7782492	50	400
Silver[1]	7440224	7 (GW-3) 40 (GW-1)	100
Thallium	7440280	2	8
Vanadium	7440622	50	400
Zinc	7440666	900 (GW-3) 2000 (GW-1)	2500
1. Requires addition of HCL for analysis. See SW-846 method 6020A, Section 7.1			

2.0 Data Usability Assessment for Method 6020A

Overall data usability is influenced by uncertainties associated with both sampling and analytical activities. This document provides detailed quality control requirements and performance standards for SW-846 Method 6020A which may be used to assess the analytical component of data usability. The sampling component of data usability, an independent assessment of the effectiveness of sampling activities to meet data quality objectives, is not substantively addressed in this document.

	Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup	WSC-CAM	Section: III D
		13 August 2004	Revision No. 2
		Final	Page 18 of 23

Title: Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 6020A, Trace Metals by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

3.0 Reporting Requirements for SW-846 Method 6020A

3.1 General Reporting Requirements for SW-846 Method 6020A

General reporting requirements for analytical data used in support of assessment and evaluation decisions at MCP disposal sites are presented in WSC-CAM-VIIA. This guidance document provides recommendations for field QC, as well as the required content of the Environmental Laboratory Report, including

> - Laboratory identification information presented in WSC-CAM-VII A, Section 2.4.1,
> - Analytical results and supporting information in WSC-CAM-VII A, Section 2.4.2,
> - Sample- and batch-specific QC information in WSC-CAM-VII A, Section 2.4.3,
> - Laboratory Report Certification Statement in WSC-CAM-VII A, Section 2.4.4,
> - Copy of the Analytical Report Certification Form in WSC-CAM-VII A, Exhibit VII A-1,
> - Environmental Laboratory case narrative contents in WSC-CAM-VII A, Section 2.4.5,
> - Chain of Custody Form requirements in WSC-CAM-VII A, Section 2.4.6

3.2 Specific Reporting Requirements for SW-846 Method 6020A

Specific QA/QC Requirements and Performance Standards for SW-846 Method 6020A are presented in Table III D-1. Specific reporting requirements for SW-846 Method 6020A are summarized below in Table III D-3 as "Required Analytical Deliverables (**YES**)". These routine reporting requirements should always be included as part of the laboratory deliverable for this method. It should be noted that although certain items are not specified as "Required Analytical Deliverables (**NO**)", these data are to be available for review during an audit and may also be requested on a client-specific basis.

3.2.1 Reporting Data for Spectral Interference Corrections

If unusual inter-element or matrix interferences are encountered, a description of any corrective measures utilized by the laboratory must be included in the Environmental Laboratory case narrative. Such measures may include use of an alternative analytical wavelength, non-standard computerized compensation, sample dilution to overcome physical or chemical interferences, use of standard additions, or other method-specific corrective actions.

Title: Routine Reporting Requirements for SW-846 Method 6020A

Table III D-3 Routine QA/QC Reporting Requirements for SW-846 Method 6020A

Parameter	Required Analytical Deliverable
Preparation of Samples and Standards	*NO*
Daily Performance Standard	*NO*
MS Tuning	*NO*
Initial Calibration	*NO*
Initial Calibration Verification (ICV)	*NO*
Initial Calibration Blank (ICB)	*NO*
Reporting Limit (RL) Calibration Check standard	*NO*
Continuing Calibration Verification (CCV)	*NO*
Continuing Calibration Blank (CCB)	*NO*
Linear Range Analysis	*NO*
Interference Check Standards (ICS-A and -B)	*NO*
Method (Preparation) Blank	*YES*
Laboratory Control Standard (LCS)	*YES*
LCS Duplicate	*YES*
Project Specific Matrix Spike Sample (MS)	*YES (if requested by data user)*
Project Specific Matrix Spike Duplicate (MSD)	*YES (if requested by data user)*
Project Specific Matrix Duplicate (MD)	*YES (if requested by data user)*
Dilution Test	*NO*
Internal Standards (Percent Recoveries)	*NO*
General Reporting – sample specific reporting limits	*YES*

Title: Regulatory Limits for Metals Under 310 CMR 40.0000

4.0 Regulatory Limits for Metals under 310 CMR 40.000

MCP Reportable Quantities together with the most stringent (lowest) Reportable Concentrations (RCs) and Method 1 Standards for metals routinely analyzed using SW-846 Method 6020A are presented in Table III D-4.

Metal	RQ Pounds	RC GW-1 mg/L - (ppm)	RC S-1 mg/kg - (ppm)	Method 1 Groundwater[1] ug/L - ppb	Method 1 Soils[2] ug/g - ppm
Aluminum	NQ	NP	NP	NS	NS
Antimony	50	0.006	10	6	10
Arsenic	1	0.05	30	50	30
Barium	100	2	1000	2000	1000
Beryllium	5	0.004	0.7	4	0.7
Cadmium	5	0.005	30	5	30
Calcium	10	NP	NP	NS	NS
Chromium (III)	100	0.1	1000	100	1000
Chromium (VI)	100	0.1	1000	50	200
Cobalt	50	5	500	NS	NS
Copper	100	10	1000	NS	NS
Iron	NQ	NP	NP	NS	NS
Lead	5	0.02	300	15	300
Lithium	10	1	100	NS	NS
Magnesium	10	NP	NP	NS	NS
Manganese	NQ	NP	NP	NS	NS
Mercury	1	0.001	20	2	20
Nickel	10	0.08	300	80 (GW-3)	300
Phosphorous	1	NA	NA	NS	NS
Potassium	10	NA	NA	NS	NS
Selenium	10	0.05	400	50	400
Silver	50	0.007	100	7 (GW-3)	100
Sodium	5	NA	NA	NS	NS
Thallium	50	0.002	8	2	8
Vanadium	50	0.05	400	50	400
Zinc	50	0.9	2500	900 (GW-3)	2500

1. Method 1 Groundwater – GW-1 Category unless otherwise noted
2. Method 1 Soils – Category S-1/GW-1 in all cases
RQ – Reportable Quantity
RC – Reportable Concentration for Groundwater (GW-1) and Soils (S-1)
NQ – No Reportable Quantity (RQ) promulgated by the Department
NP – No Reportable Concentration (RC GW-1 or RC S-1) promulgated by the Department
NS – No MCP Method 1 Standard has been promulgated by the Department.

Sample Preservation, Container and Analytical Holding Time Specifications for Surface Water, Groundwater, Soil and Sediment Samples Analyzed for Metals by ICP-MS in Support of MCP Decision Making

Sample preservation, container and analytical holding time specifications for surface water, groundwater, soil, sediment and wastes matrices for metal analyses conducted in support of MCP decision-making are summarized below and presented in Appendix VII-A of WSC-CAM-VII A, Quality Assurance and Quality Control Guidelines for Sampling, Data Evaluation, and Reporting Activities for the Massachusetts Contingency Plan (MCP). Additional guidance may be found in SW-846, Chapter Three

Matrix	Sample Container(s) [1]	Preservative	Holding Time [2]
Total Metals Groundwater and Surface Water	(1) 1-L Polyethylene Bottle for Total Metals	HNO_3 to pH < 2,	180 days: all metals except mercury 28 days: mercury
Dissolved Metals Groundwater and Surface Water	(1) 1-L Polyethylene Bottle for field-filtered sample for Dissolved Metals	Filter (0.45 μm) on site; or at the laboratory (*prior to acid preservation*) within 24 hours of collection HNO_3 to pH <2,	180 days: all metals except mercury 28 days: mercury
Suspended Metals Groundwater and Surface Water	Submit Suspended Solids on Filter to Laboratory	Filter on site Filter 100 – 500 ml of unpreserved sample	180 days: all metals except mercury 28 days: mercury
Soils and Sediments	(1) 4-ounce glass jar	Cool, 4°C	180 days: all metals except mercury 28 days: mercury
Concentrated Waste Samples	125 mL wide mouth glass or plastic	Cool to 4°C	180 days: all metals except mercury 28 days: mercury

1 The number of sampling containers specified is not a requirement. For specific analyses, the collection of multiple sample containers is encouraged to avoid resampling if sample is consumed or compromised.
2 From date of sample collection.

Title: Methods for Sample Digestion or Preparation for Metal Analyses by ICP-MS

SW-846 Method	Method Description
3005	Method prepares groundwater and surface water samples for total recoverable and dissolved metal determinations by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO prior to metal determination.
30l0	Method prepares waste samples for total recoverable metal determinations by FLAA, ICPAES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.
3015	Method prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total recoverable metal determinations by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.
3031	Method prepares waste oils, oil sludges, tars, waxes, paints, paint sludges and other viscous petroleum products for analysis by FLAA, GFAA, and ICP-AES. The samples are vigorously digested with nitric acid, sulfuric acid, hydrochloric acid, and potassium permanganate prior to analysis.
3040	Method prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content
3050	Method prepares waste samples for total recoverable metals determinations by FLAA and ICP-AES, or GFAA and ICP-MS depending on the options chosen. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.
3051	Method prepares sludges, sediments, soils and oils for total recoverable metal determinations by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to the representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to metals determination.
3052	Method prepares siliceous and organically based matrices including ash, biological tissue, oil, oil contaminated soil, sediment, sludge, and soil for total analysis by FLAA, CVAA, GFAA, ICPAES, and ICP-MS. Nitric acid and hydrofluoric acid are added to a representative sample in a fluorocarbon digestion vessel and heated in a microwave unit prior to analysis

Quality Control Flow Chart for SW-846 Method 6020A (ICP-MS) Analysis

SW-846 Method 6020A
Inductively Coupled Plasma – Mass Spectrometry

Quality Control Flow Chart

Start

7.1 Use appropriate digestion procedure (Chapter Three.)

7.2 Initiate operating configuration of instrument computer.

7.3 Set up and stabilize instrument.

7.4 Set operating conditions as recommended.

7.5 Perform mass calibration and resolution checks.

7.6 Calibrate the instrument for the analytes of interest.

7.7 Monitor all masses that could affect data quality, as recommended.

7.8 Verify calibration with ICV.

Are results outside +/- 10% range of actual value?

Yes → Readjust instrument per manufacturers' recommendations.

No → 7.9 Flush system and analyze sample.

7.9 Analyze check standard and calibration blank after each 10 samples.

Does response exceed calibration curve range?

Yes → 7.10 Dilute extract.

No → 7.11 Calculate concentration.

Stop

From SW-846 Method 6020B